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A Diode Laser Sensor for Measurement
of Hydrogen Chloride Gas

Phase I Final Technical Report

Prepared Under Contract No. DAAD07-87-C-0036
for U.S. Army White Sands Missile Range

Prepared by

Alan C. Stanton and Joel A. Silver
Southwest Sciences, Inc.
1570 Pacheco St., Suite E-11
Santa Fe, New Mexico 87501

Alan C. Stanton
Alan C. Stanton, President

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The near-infrared diode laser absorption techniques studied in this program may also be applied to the measurement of many other gases in such applications as toxic gas detection, on-line monitoring of industrial processes, pollutant monitoring, and atmospheric reasearch.

PROJECT SUMMARY

Large quantities of hydrogen chloride (HCl) gas are emitted during the launch of certain types of missiles. This toxic exhaust product can pose a significant safety hazard to launch-area personnel, and there is a critical need for monitoring instrumentation that can provide real-time measurements of HCl in launch areas. The purpose of this study is to investigate a new instrumentation concept for HCl measurement, based on absorption of near-infrared radiation from inexpensive commercial laser diodes which are used in the lightwave communications industry. The results of Phase I show that the concept exceeds program requirements for sensitivity and time response.

In the Phase I research, breadboard instrumentation incorporating a standard commercial InGaAsP laser diode and an optically stable multiple pass absorption cell was used to measure the HCl spectroscopic parameters needed to calibrate the technique and determine the conditions for optimum sensitivity. The technique of two-tone FM spectroscopy employing high frequency laser modulation was then used for direct assessment of the sensitivity limits in measuring low concentrations of HCl in air. The results were compared with a detailed model of the two-tone FM signal in order to analyze the sensitivity for an optimized system.

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The near-infrared diode laser absorption techniques studied in this program may also be applied to the measurement of many other gases in such applications as toxic gas detection, on-line monitoring of industrial processes, pollutant monitoring, and atmospheric research.

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1. INTRODUCTION

Large quantities of hydrogen chloride (HCl), in both gas and liquid aerosol forms, are emitted during the launch of certain types of missiles. This toxic exhaust product can pose a significant safety hazard to launch-area personnel that may persist for extended time periods following the launch. Studies of HCl contamination from NASA Space Shuttle launches have shown that local HCl gas concentrations in the launch area can potentially exceed the ceiling concentration of 5 parts-per-million (ppm) for hours after the launch, due to revolatilization of deposited HCl aerosol.¹ This concentration limit of 5 ppm is recognized both by the Occupational Safety and Health Administration and by the American Conference of Government Industrial Hygienists as a level that should not be exceeded even instantaneously for human occupational exposure.^{1,2} Potentially dangerous concentrations of HCl have been measured during launches of other missiles as well as during static rocket firings.² Thus a critical need exists for monitoring instrumentation that can provide sensitive and real-time measurements of HCl in launch areas.

Existing environmental monitoring instrumentation for measurement of HCl has been reviewed by Swoboda and Naugle.² Although many passive methods exist for measurement of HCl (e.g., dosimeter tubes, electrets, bubblers/impingers, GC tubes, etc.), these methods require subsequent analysis, and then indicate only the integrated exposure rather than instantaneous concentrations. Existing instrumentation for real-time measurement of HCl gas concentrations include chemiluminescent analyzers and nondispersive infrared (NDIR; also called gas correlation) spectrometers.

Chemiluminescent HCl monitors manufactured by GEOMET, Inc. have been used in the NASA Launch Vehicle Effluent Monitoring Program.³ These instruments are based on luminol chemiluminescence resulting from reactions with the products formed when HCl reacts with a bromide-bromate coating on the inlet tube walls. This type of instrumentation has good sensitivity, although several other species can cause positive (enhanced apparent HCl signal) or negative (reduced apparent HCl signal) interferences. The major drawback of the chemiluminescent monitor is its relatively slow time response. At 50 ppm, the time response (defined as the time for the signal to rise to 90% of its

final value) is reported as 0.5 second, degrading to 5 seconds at 5 ppm and 20 seconds at 0.1 ppm.³ The long response time at low concentrations is apparently due to scavenging of HCl by the inlet tube until its surface is fully passivated. Since surface reactions of HCl are required to generate the chemiluminescence, the response time probably cannot be improved without significant loss in sensitivity. For the present application, where a response time of less than one second is needed, the chemiluminescent monitor does not meet the requirements.

Nondispersive infrared or gas correlation analyzers have been used for airborne measurements of HCl gas in studies of Space Shuttle exhaust clouds.⁴ These instruments measure infrared absorption in the fundamental vibrational-rotational band of HCl ($\sim 3.5 \mu\text{m}$) using a broadband infrared source (such as a Nernst glower or quartz lamp) and an HCl gas filter to enhance the specificity of the instrument to HCl. The minimum detectable HCl concentration (signal-to-noise ratio of unity with a one second time constant) for this instrument is reported as 0.5 ppm.⁵ This means that for concentrations of 5 ppm, the uncertainty is 10%, and worsens at lower HCl levels. In addition, some interference due to other atmospheric gases such as H_2O and certain hydrocarbons would be expected since these gases have absorption lines within the instrument's gas filter bandwidth, defined by the HCl absorption linewidths. Since many of these gases are also important constituents of missile exhaust, such interference may be significant. Present requirements are not met by NDIR or gas correlation instruments, due to their poor sensitivity and potential for interference problems.

In this Phase I research program, we have studied a new instrumentation concept for field measurement of HCl gas concentrations, based on absorption of near-infrared ($\sim 1.2 \mu\text{m}$) radiation from InGaAsP laser diodes. This approach overcomes the time response limitations of the chemiluminescent analyzers because HCl is measured directly, rather than via sequential surface reactions; therefore a high sampling throughput is possible. The approach also overcomes the sensitivity and interference limitations of gas correlation analyzers, because an intense, very high resolution light source is used that can be tuned to wavelengths where only HCl and none of the interfering gases absorb infrared radiation. Moreover, this approach uses inexpensive and

highly reliable components which can be configured in a compact package suitable for untended operation at ground sites near launch areas or for airborne HCl measurements. The instrumentation could also be configured in a fiber-optic network for centralized monitoring of HCl concentrations near launch sites.

The primary result of Phase I is the demonstration of very high detection sensitivity for HCl using laboratory instrumentation based on 1.2 μm diode laser absorption. A sensitivity level of 3 ppm HCl in air at 50 torr was demonstrated by direct measurement using the nonoptimized Phase I instrumentation. Substantial additional improvements in sensitivity can be realized by using a single mode (single frequency) laser rather than the multimode laser used in Phase I, by increasing the absorption path length obtained in the multiple pass cell, by operating the system at a higher pressure, and by optimization of the laser modulation techniques. These improvements would be expected to increase the sensitivity by a factor of 100, so that real-time detection of HCl concentrations below 0.1 ppm would be easily achieved with a near-infrared diode laser monitoring instrument.

2. PHASE I RESEARCH OBJECTIVES

The primary objective of the Phase I research was to demonstrate a simple method utilizing a standard, commercially available diode laser source for the accurate measurement of hydrogen chloride gas concentrations over a range pertinent to missile launch sites. Important criteria for an eventual field instrument include rapid response, good accuracy, sensitivity of 0.1 ppm, reliability, compact optical layout, and direct electronic readout. The essential research issues addressed in Phase I included:

1. Using a standard commercially available InGaAsP diode laser, infrared line parameters (absorption line strength and pressure broadened linewidths) were measured for an appropriate HCl absorption line near 1.2 μm in order to provide data for absolute calibration of the measurement technique and to demonstrate the sensitivity of the technique.
2. Accurate measurement, data collection, and calibration techniques were studied and approaches for optimization were identified. Such techniques should permit the achievement of sensitivity levels better than 0.1 ppm HCl with fast time response. A goal of the program, as defined in the original solicitation, is a time response of less than one second for the instrumental reading to reach 90% of its value.

Our research has been directed toward answering the following critical questions:

- (1) Can inexpensive, commercially available diode lasers be applied to the routine measurement of atmospheric hydrogen chloride vapor in a rugged, compact instrument having high accuracy, rapid response, and reliable calibration characteristics?
- (2) Can high frequency laser modulation techniques be utilized to obtain the high sensitivity required for measurement of optical absorption and thereby permit the rapid and accurate measurement of HCl gas at sub-ppm concentrations?

3. RESEARCH APPROACH

3.1 Overview of Experiments Performed

As outlined in the discussion of objectives in Section 2, the Phase I experiments were aimed at quantifying the detection limits for measurement of HCl by near-infrared diode laser absorption near $1.2\text{ }\mu\text{m}$. Two types of measurements were performed. The first type of experiment involved direct measurement of the absorption cross section (line strength) and broadening parameters for a selected absorption line of HCl. An accurate knowledge of these parameters is necessary for calibration of the technique and to determine the optimum system design (absorption cell size, measurement pressure, etc.). The second type of experiment was an assessment of the detection sensitivity obtained in measuring low concentrations (including levels below 10 ppm) of HCl in air. For these latter experiments, the measurements were made using the technique of two-tone FM spectroscopy, in which the diode laser is modulated at high frequencies in order to overcome the effects of low-frequency laser noise. All experiments were performed using a laboratory breadboard setup, employing a multimode laser diode, a multiple pass absorption cell, and a room temperature detector. The experimental results were compared with a detailed model of the two-tone FM signal in order to assess the system performance vs. theoretical detection limits and to analyze the sensitivity for an optimized system.

3.2 Description of Optical System

3.2.1 Diode Laser

The diode laser used in the Phase I study is a commercial InGaAsP device manufactured by Mitsubishi (Model ML8701) for use in near-infrared fiber optic communications systems. This laser is a standard mass-produced commercial item, and no additional specifications pertinent to the present spectroscopic application were imposed in purchasing the laser. This laser operates multimode (multiple longitudinal modes) with a threshold current at room temperature of 16 mA. The laser may be coarsely tuned (tuning rate of approximately $0.4\text{ nm }^{\circ}\text{C}^{-1}$) by varying its temperature over an operating range of -20 to $+70\text{ }^{\circ}\text{C}$. This temperature range was found to correspond to

wavelength tuning from 1196 to 1232 nm, by measurement with a monochromator. This spectral range broadly overlaps the P branch of the HCl second overtone ($v=3 \leftarrow v=0$) band. High resolution wavelength tuning is accomplished by varying the laser diode injection current above threshold. The instrumental width of each laser mode was found to be small relative to the spectral width of the HCl absorption lines, so that full spectral resolution of the detailed molecular line shapes is achieved.

The laser as received is packaged in a hermetically-sealed window can (9 mm dia.). This package also contains a photodiode for laser power monitoring from the rear facet of the laser diode. For the Phase I experiments, the laser package was housed in a commercial laser diode mount (ILX Lightwave Model LDM-4412) which is designed for precision-controlled thermoelectric cooling of the laser (two TE coolers are contained in the mount). This mount also contains a 0.5 NA single-element lens for collimation of the laser output beam. The approximate size of the mount is 2" (depth) x 4" (width) x 4" (height).

The laser temperature is regulated by a commercial controller supplied by ILX Lightwave (Model LDT-5910). This unit monitors the resistance of a calibrated thermistor epoxied to the laser mounting plate and adjusts the current to the TE coolers to achieve a desired setpoint temperature. The temperature stability of this system is better than 0.01 °C.

The current source used in Phase I for high resolution tuning of the laser diode was a Spectra-Physics Model SP-5820 precision diode laser power supply. While this supply is designed for use with middle infrared lead-salt diode laser systems, it is also suitable for use with the near-infrared InGaAsP lasers. Inexpensive precision current sources specifically intended for use with InGaAsP lasers are readily available.

3.2.2 Multiple Pass Cell

The multiple pass absorption cell used in the Phase I study is designed to provide a compact, yet sufficiently long, optical path for accurate, rapid response measurement of HCl gas at concentrations of concern in missile launch areas. Air is drawn continuously through the cell using a small vacuum pump. A throttle valve at the inlet is used to reduce the pressure below 100 torr,

so that pressure broadening is minimized. As discussed in Section 4.2.4, a higher sampling pressure will yield somewhat larger signals, and atmospheric pressure operation of the cell is feasible. The residence time of an air sample in the cell used in Phase I (pumping speed of $0.4 \text{ liters sec}^{-1}$) is less than 2 seconds, permitting fast response of the system to fluctuations in HCl concentration. A compact system with higher throughput could be easily designed to achieve response times under 1 second. The inlet lines and cell can be maintained at a constant ($\pm 1^\circ \text{C}$) temperature. By slightly heating the cell relative to ambient conditions, any condensation of water vapor inside the cell or sampling lines, which might lead to high rates of surface adsorption of HCl, is avoided. In addition, by always performing the absorption measurements at the same controlled temperature, no temperature corrections are required in the spectroscopic parameters (line strength and broadening coefficients) used in determining HCl concentrations from the measured laser absorption.

The multiple pass cell is based on an optical design by Herriott.⁶⁻⁹ The optical design of the cell is illustrated in Fig. 1. The mirrors which define the optical path are spherical and of equal focal length, f . The incoming beam passes through a hole in the front mirror at a small angle γ . The separation of the mirrors is set between f and $2f$. With this constraint, it can be shown⁹ that for particular values of mirror separation and γ , and for $N = 2(j+2)$ passes ($j=\text{integer}$), the outgoing beam will emerge through the entrance hole at the same point as it entered, but with an angle of $-\gamma$. Initially collimated, the beam is periodically focused and recollimated so that, upon exiting the system, it again is collimated and has the same diameter with which it entered the cell. The pattern of spots on each mirror forms an ellipse, which becomes more circular as $N \rightarrow \infty$ (i.e., as $d \rightarrow 2f$). A particular advantage of the Herriott design is that slight optical misalignments (in mirror tilt, mirror separation, or entrance angle) have negligible effects on the total path length ($< 0.5\%$) or output beam position ($< 3\%$).⁹

In the Phase I study, 4.6-cm diameter gold-coated mirrors of 25 cm focal length were used for the Herriott cell optics. The front mirror was notched in order to pass the entering and exit beams. This mirror was fixed in

position or the front end flange of the cell, while the rear mirror was mounted on a push-rod assembly which extended from the cell through a vacuum coupling. This assembly was used to position the rear mirror over a range of axial locations in order to vary the number of passes through the cell. Aside from this axial adjustment, no other adjustments are required for the Herriott cell optics. For most measurements in this study, the cell was set for either 30 or 34 passes, corresponding to total absorption path lengths of 1347 and 1546 cm, respectively. The cell was constructed of commercially available stainless steel vacuum tees (MDC Vacuum Products), with an inside diameter of approximately 4.7 cm. The cell was instrumented with a capacitance manometer (MKS 127A, 0-10 torr, or MKS 227A, 0-100 torr) for pressure measurements.

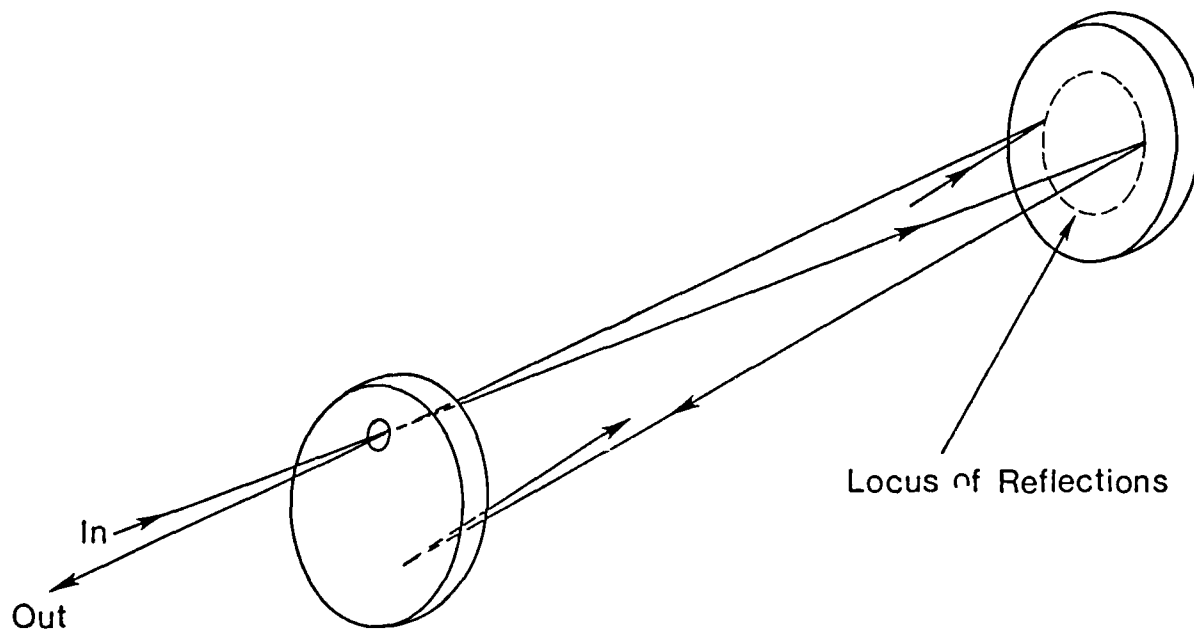


Figure 1. Optical Design of the Multiple Pass Herriott Cell.

Although Herriott cell optics have been used in a number of prior laser spectroscopy experiments,⁸ the multiple pass optical design almost universally used in diode laser spectroscopy with mid-infrared lasers has been the conventional White cell.^{10,11} The principal advantage of the Herriott cell is that the design is particularly insensitive to slight misalignment and should be easily adaptable to optical fiber coupling of the laser beam. These characteristics permit the design of exceptionally simple and stable optical configurations for field use. By contrast, White cells are very sensitive to misalignment and require nine optical adjustments for three mirror elements.

3.2.3 Optical Layout

The optical layout used in the Phase I studies is shown in Fig. 2. The approximately circular collimated diode laser beam emerging from the 0.5 NA lens is reduced from ~4 mm to ~2 mm diameter using a pair of spherical mirrors. The narrow collimated beam is directed into the Herriott cell, and the beam emerging from the cell is focused onto a room temperature germanium photodiode using a 7.5 cm focal length mirror. A mechanical chopper is placed in the beam before it enters the cell to permit lock-in detection of the signal.

The germanium photodiode (Judson J16-LD) has a 0.25 mm diameter active area and is mounted directly on a BNC connector. For these experiments, the photodiode was operated at zero bias, with a bandwidth of at least 100 MHz. The photodiode current (approximately 0.5 A W^{-1} at $1.2 \text{ }\mu\text{m}$) was converted to a voltage using a wide bandwidth (200 MHz) transimpedance amplifier with an input impedance of $50 \text{ }\Omega$ and a voltage gain of 18. A relatively high bandwidth (greater than 10 MHz) is required for the FM detection techniques used in this study.

Although this Phase I setup utilized conventional optics, a system employing fiber optics to transmit the laser signal to the cell and from the cell to the detector could be easily designed in future instrumentation. In particular, integrated laser/optical fiber and detector/optical fiber packages are readily available, as are fiber optic choppers if required. The use of fiber optics in field instrumentation is desirable because it eliminates the effects of adverse weather conditions (blowing dust, precipitation, etc.)

which can damage ordinary optics or degrade transmission. In addition, the use of fiber optics would permit the design of a system requiring absolutely no optical adjustments. Conceivably, the absorption cell could even be remotely located from the laser source and detector, since the fiber transmission losses at $1.2\text{ }\mu\text{m}$ are low even for distances of several kilometers.

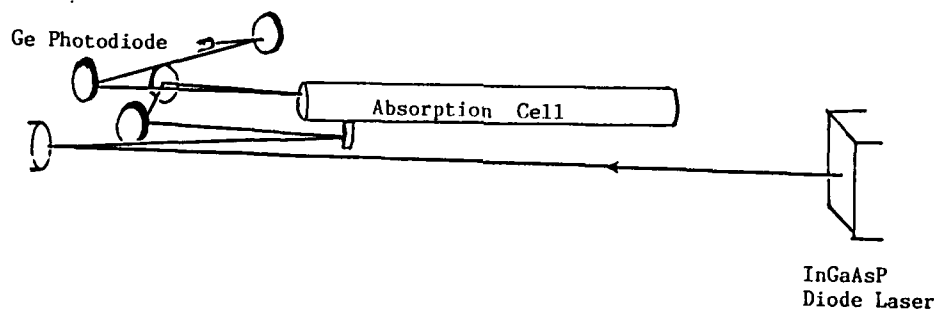
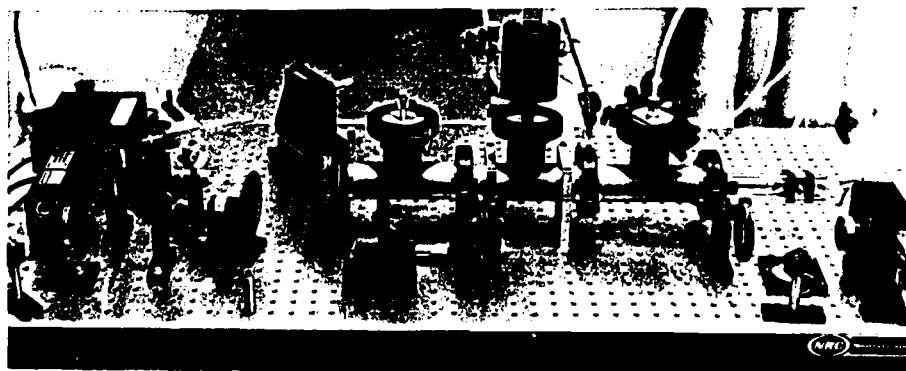


Figure 2. Optical Layout Used in Phase I Experiments.
a) Photograph of system; b) Outline of major components.

3.3 Experimental Methods

3.3.1 Overview

The experimental methods used in the Phase I research are described in this section. The approaches used in measurement of HCl absorption line parameters are first described. The theory and experimental setup for two-tone FM spectroscopy, which permits the attainment of very high detection sensitivity for absorption measurements, are then discussed in detail. Finally, we describe the methods used to characterize the detection sensitivity of the Phase I instrumentation under conditions of low HCl concentrations.

3.3.2 Measurement of HCl Absorption Line Parameters

A portion of the Phase I research was devoted to accurate laboratory measurement of the infrared line strength (integrated absorption cross section) and air broadening coefficient for an HCl absorption line that was identified as suitable for launch area monitoring applications. Measurement of these line parameters provides the basic spectroscopic information required for quantitative calibration of HCl data obtained with the diode laser absorption method. In addition, these data are crucial in determining the best system design for optimum measurement sensitivity.

For the measurements of infrared line strength, hydrogen chloride gas (Airco VLSI grade, stated purity of 99.999%) was used without further purification. Previous workers who studied the HCl fundamental absorption band¹² had found a large impurity, presumed to be H₂, which did not freeze out of their commercially-obtained HCl sample at liquid nitrogen temperature. We checked for such an impurity by trapping the HCl from the cylinder at liquid nitrogen temperature. Measurements of residual pressure in the trap showed that any noncondensable impurity must be less than 0.1% of the sample.

For the line strength measurements, pure HCl was pumped continuously through the absorption cell and diode laser transmission scans were made as the HCl pressure in the cell was varied. A computer system for laser control and data acquisition as described below was used for these scans. For these measurements, the pressure was maintained at low values (typically less than

2.0 torr) where pressure broadening is insignificant. The zero transmission level was established for each series of measurements from a scan under conditions of high HCl pressure (nearly atmospheric pressure), where the absorption is optically black. Since the laser was operating with several different longitudinal modes, this measurement established the fraction of the total laser power contained in the mode coincident with the HCl absorption wavelength. This fraction corresponded to approximately 22 percent at the center of the HCl absorption line, and no variations in this power fraction were observed over several days of experiments.

For measurements of line broadening in air, a static fill of HCl at 2 torr was introduced to the cell. Dry air (Airco, H₂O less than 10 ppm) was added to the cell and transmission scans were made over the line profile for broadening gas pressures ranging from 0 to 110 torr.

The relative frequency scale used in analyzing these scans was based on the assumption of negligible instrumental broadening, so that the measured absorption linewidth in the low pressure limit corresponds to the true Doppler linewidth. This assumption was checked by comparing the direct absorption linewidth with the two-tone FM line shape. (The FM technique is described in detail in the next section.) The separation of line shape minima in the FM spectra is sensitive to any instrumental broadening effects in this modulation regime, because the modulation frequencies are comparable to the Doppler linewidth (516 MHz full width at half maximum). A comparison with simulated FM line shapes showed that any instrumental broadening of the linewidth was less than 5 percent. This result implies an intrinsic laser linewidth of less than 160 MHz, since the laser linewidth and molecular linewidth add in quadrature to first approximation.

For measurements of line strength and broadening parameters, interfacing of the laser control and data acquisition functions with a computer was important in order to obtain data in digital form for subsequent analysis. A Texas Instruments Business Pro Computer (an 8 MHz 80286-based microcomputer compatible with the IBM AT) equipped with a GPIB (IEEE-488) instrumentation interface card (National Instruments) was used in combination with a Stanford Research SR530 lock-in amplifier to achieve the desired interfacing. The SR530 lock-in is fully controllable with the GPIB interface. The output of

one of the two 13-bit D/A converters provided with the lock-in was used as a computer-scannable current source to add to a constant dc bias current supplied by the Spectra-Physics diode laser power supply. In this arrangement, the Spectra-Physics supply is used to set a dc current corresponding to a desired laser frequency for the start of a spectral scan. The laser current is then scanned in steps by the SR530 D/A converter with a resolution and total scanning interval set by the user over the GPIB interface. The measurements of line strength and line broadening were performed in a direct transmission mode, in which the diode laser beam is mechanically chopped and the synchronously detected optical signal measured by the lock-in is transferred to the computer at each current step using the GPIB interface.

The line strength and line broadening data were analyzed using a Voigt profile fitting routine. This routine is a graphics-based user-interactive program implemented on the TI Business Pro computer used to acquire the spectroscopic data. The analysis begins with two preliminary procedures to obtain least squares fits of the laser intensity background and the zero transmission background to third-order polynomials. Based on these fits, the variation of laser background intensity (i.e., the 100% transmission level, I_0) is subtracted from the scan. A nonlinear least-squares procedure is then used to fit the absorbance ($\ln(I_0/I)$) to a Voigt line shape, using the approximations developed by Hui et al.¹³ for computation of the Voigt profile. This fitting procedure yields values for the integrated absorbance and the Gaussian and Lorentz contributions to the linewidth. At higher broadening gas pressures, the Gaussian linewidth was fixed in the fitting procedure at the value determined in the low pressure limit. The final experimental values for line strength and broadening coefficient were obtained by plotting the integrated absorbance versus hydrogen chloride concentration (the slope of this linear plot yields the line strength) and the Lorentz linewidth versus foreign gas (air) pressure (where the slope yields the broadening coefficient).

3.3.3 Two-Tone FM Spectroscopy

The high sensitivity detection technique studied in this program is termed optical heterodyne (FM) spectroscopy.¹⁴⁻¹⁶ This method uses rf modulation of the diode laser injection current to generate weak frequency sidebands about the carrier (laser) frequency. When the laser is scanned through an absorption feature, the beat frequency signal generated by the sidebands is detected. Because the noise spectrum of diode lasers falls off significantly above 10 to 100 kHz,¹⁷ the ultimate attainable sensitivity using FM detection should be limited only by the noise of the detector, which for modest laser intensities is the detector shot-noise generated by the incident laser beam.

In the case of two-tone FM spectroscopy,¹⁸⁻²⁰ the laser is modulated by a closely spaced pair of frequencies (495 and 505 MHz in this study), and detected at the 10 MHz beat frequency. The advantage of this approach is that a relatively inexpensive detector can be used, whereas above 10 MHz (as would be required for a single-tone rf modulation) the detectors become increasingly expensive. A brief description of two-tone detection is given in the remainder of this section, followed by a summary of the electronic setup needed to carry out these measurements.

3.3.3.1 Theory

If an rf field consisting of two closely spaced frequencies ω_1 and ω_2 ²¹ is superimposed on the carrier (laser) frequency, the optical field becomes¹⁹

$$E(t) = E_0(t) \cdot [1 + M_1 \sin(\omega_1 t + \psi_1)] \cdot [1 + M_2 \sin(\omega_2 t + \psi_2)] \\ \times \exp[i\beta_1 \sin \omega_1 t + i\beta_2 \sin \omega_2 t] . \quad (1)$$

The term $E_0(t)$ is the time-dependent electric field of the unmodulated laser beam. The factor β is the frequency modulation index, which represents how well the rf modulation is coupled to the carrier frequency. The exponential terms lead to the introduction of frequency sideband pairs about the laser frequency ω_0 . The pre-exponential terms in brackets represent amplitude modulation factors arising from the nonuniformity in laser intensity over the frequency range spanned by these sideband pairs. This effect carries some of

the intrinsic low frequency laser noise into the FM signal and introduces a small amplitude modulation at frequencies ω_1 and ω_2 . The factor M (the amplitude modulation index) is a measure of the degree of this residual amplitude modulation. The phase difference between the AM and FM modulation is ψ . Because ω_1 and ω_2 are very closely spaced relative to the absorption linewidths, we can approximate $M_1 \approx M_2 \equiv M$, $\psi_1 \approx \psi_2 \equiv \psi$, and $\beta_1 \approx \beta_2 \equiv \beta$.

Now consider the transmission of the laser through a sample of gas. At each frequency component, the complex transmission is

$$T_n = \exp[-\delta(\omega) - i\phi(\omega)] , \quad (2)$$

where $\delta(\omega)$ is the electric field amplitude attenuation coefficient and $\phi(\omega)$ is the optical phase shift proportional to the change in refractive index of the sample. Absorption is usually discussed in the context of attenuation of the light *intensity*. Since this intensity is related to the optical field by

$$I(t) = \frac{c}{8\pi} |E(t)|^2 , \quad (3)$$

the intensity attenuation varies as $|T_n|^2$. The absorbance $\alpha(\omega) = \sigma(\omega)N\ell$ is equivalent to $2\delta(\omega)$, where $\sigma(\omega)$ is the frequency-dependent absorption cross section, N the gas number density, and ℓ the absorption path length. If one detects the signal at the beat tone Ω (difference frequency between ω_1 and ω_2) by homodyne-detecting this signal using a local oscillator at frequency Ω in a double-balanced mixer, the IF output of the mixer is a dc signal which can be expressed as

$$I_\Omega = 2I_0 \sum_{n,m} r_n r_m r_{n-1}^* r_{m+1}^* \cdot \exp[-\alpha(\omega_0 + (n+m)\omega_m)] = 2I_0 [Q(\alpha) + M^2] , \quad (4)$$

where the exponential terms are the absorption line shapes for the carrier frequency and higher order $(n+m)$ harmonics of the modulation frequency. The r coefficients are Bessel functions related to M and β by

$$r_n(\beta, M, \psi) = \sum_{k=-1}^1 a_k J_{n-k}(\beta), \quad (5)$$

with $a_0 = 1$, and $a_{\pm 1} = \pm(M/2i)\exp(\pm i\psi)$. In the absence of absorption, the signal intensity (baseline) is simply $2I_0M^2$. This allows us to define $2I_0Q(\alpha)$ as the absorption component of the waveform. In the case where $M \ll \beta < 1$, and α is much less than unity, only the absorptions at the carrier frequency ($\alpha_0 \equiv \alpha(\omega_0)$) and first upper and lower sidebands ($\alpha_{\pm} \equiv \alpha(\omega_0 \pm \omega_m)$) contribute significantly to the signal, so that

$$I_Q = I_0 \cdot [\beta^2(\alpha_0 - \frac{1}{2}\alpha_- - \frac{1}{2}\alpha_+) + 2M^2] . \quad (6)$$

This waveform consists of a positive central peak at ω_0 and negative peaks at $\pm\omega_m$ of approximately half the central peak amplitude. The dc offset is $2I_0M^2$. For modulation frequencies much greater than the absorption linewidth, these peaks are well separated. As the line shapes are pressure-broadened, or if lower frequencies are used, then the wings of the positive and negative line shape components increasingly cancel one another, resulting in a smaller signal strength.

The signal to noise ratio for two-tone FM detection using infrared detectors can be expressed as¹⁹

$$SNR = \frac{CNR_0 |Q(\alpha)|^2}{1 + CNR_0/SBR_0} , \quad (7)$$

where

$$SBR_0 \equiv \frac{\langle P \rangle^2}{\sigma_P^2 M^4} , \quad (8)$$

and

$$CNR_0 \equiv \frac{(\frac{e\eta}{h\omega_0})^2 2\langle P \rangle^2}{2e\Delta f \left[(\frac{e\eta}{h\omega_0}) \langle P \rangle (1 + \frac{M^2}{2})^2 + \frac{2kT_N}{eR_L} \right]} . \quad (9)$$

The SBR_0 term contains amplitude noise originating in the laser and reflects the carryover of this low frequency laser noise into the FM signal. This is

called the laser excess noise, and is defined as the square of the ratio of mean laser power $\langle P \rangle$ to the variance σ_P of the detected laser power.

The CNR_0 term consists of shot noise from the detected laser field and from thermal noise from the preamplifier and detector. The detection bandwidth in units of Hz is Δf and the quantum efficiency of the detector is η . The detector preamplifier impedance and effective temperature are denoted by R_L and T_N , respectively.

When ω_m is much greater than the absorption halfwidth (that is, the FM peaks are well separated) then Eq. (7) can be solved explicitly for α_{\min} , assuming that just the $n = 0$ term in $Q(\alpha)$ contributes to the signal at the line center frequency. Thus the minimum detectable absorption for a SNR of unity is¹⁹

$$\alpha_{\min} = \frac{1}{\sum_n J_n^2(\beta) J_{n-1}^2(\beta)} \left[\frac{1}{CNR_0} + \frac{1}{SBR_0} \right]^{\frac{1}{2}}. \quad (10)$$

However, for the studies presented in this report, the peaks are not entirely resolved because ω_m is comparable to the molecular linewidth, and higher order terms in $Q(\alpha)$ must be considered in contributing to α_{\min} . This requires a parametric solution of Eq. (7) to find the value of α corresponding to a signal to noise ratio of unity. In either case one can show that the optimum sensitivity is obtained for $\beta \approx 1.15$.

As part of the Phase I study, we developed software on the Texas Instruments AT-compatible microcomputer which calculates and plots the two-tone FM signal using Eq. (4). This software was used to determine the experimental values of the modulation indices β and M by comparison of the magnitude and detailed line shape of the measured FM signals with computed FM signals. A Voigt profile for the absorption line shapes is used. The theoretical signal to noise ratio, based on a parametric solution to Eq. (7), is also computed. These calculations proved extremely useful for comparison with the S/N levels which were attained in the experimental HCl measurements. In addition, the software was useful in evaluating the conditions (cell pressure, laser modulation frequency, etc.) which would optimize measurement

sensitivity in future instrumentation development. These calculations are discussed in Section 4.2.

3.3.3.2 Experimental Setup

A block diagram of the experimental FM detection system is shown in Fig. 3. The Laser Analytics diode laser current controller is used to ramp the injection current and sweep the laser frequency across the spectral feature of interest. The modulation frequencies used are 495 MHz and 505 MHz and are generated by temperature compensated crystal oscillators (Vectron, frequency stable to 0.1 ppm). The +7dBm output of a 5 MHz crystal is divided into a weak and strong component with a Mini-Circuits ZDC-10-1 directional coupler. This device splits off 30% of the signal which is frequency doubled to 10 MHz and fed to the LO port of the detector mixer (Mini-Circuits ZFM-3). The remainder of this signal is mixed (Mini-Circuits ZFM-4) with the 500 MHz oscillator signal to produce two frequencies at 495 and 505 MHz. These are passed through a 33 pF coupling capacitor into the laser injection current.

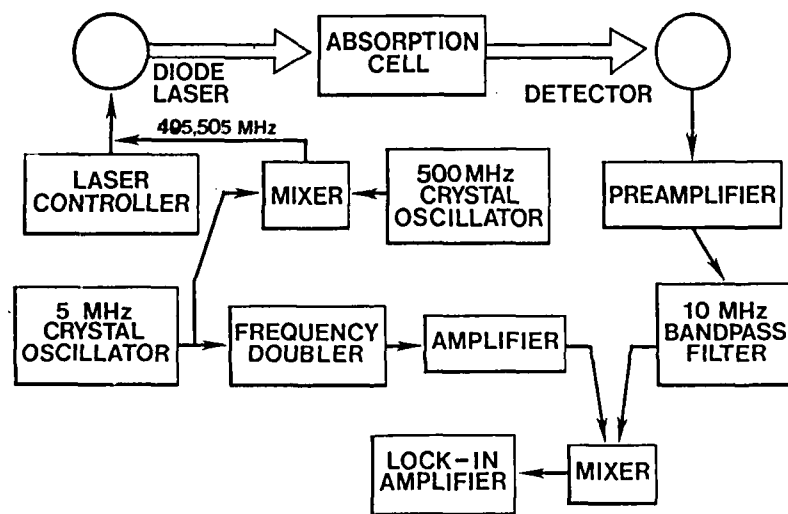


Figure 3. Block Diagram of FM Electronic Components.

No effort was made to optimize the efficiency of this coupling. The detector output is fed to the RF port of the ZFM-3 mixer. The mixer's IF output is low pass filtered (<1 MHz, K&L) and fed to a lock-in amplifier. The output of the lock-in is sent to the microcomputer through a GPIB interface, as well as an X-Y recorder, for later analysis. Despite the seeming complexity of these electronics, they are in fact quite compact, inexpensive, and simple to set up.

3.3.4 Measurement of Low HCl Concentrations

Two-tone FM spectroscopic measurements of HCl were made as a function of concentration to determine the minimum detectable HCl level, as well as to assess how the laboratory instrumentation responded to such low concentrations in terms of interferences and residual signals originating from surface outgassing, etc. Mixtures of dry air containing calibrated concentrations of HCl were flowed through the absorption cell at a total pressure of 50 torr, with a total gas residence time of approximately 2 seconds. The HCl concentrations are accurately established by separately metering the dry air and HCl flows. A two-tone FM spectral scan was recorded for each HCl concentration. Peak FM signal intensities were plotted versus HCl concentrations (in ppm) to demonstrate the linearity of this technique and to display any intercept (i.e., residual signal at nominally zero HCl in the flow), which would correspond to a signal arising from HCl outgassing from the cell walls.

In order to ensure that the trace concentrations of HCl in these experiments are very accurate, we used a dP/dt apparatus to measure the HCl flow. At the very low flows used, electronic flowmeters do not have nearly the required sensitivity or accuracy. The layout for the dP/dt system is shown in Fig. 4. All components are constructed of stainless steel. First, a 1.0-liter sample cylinder is filled to approximately 1 atm pressure with pure HCl (Airco, 99.999%). This gas is metered into the system through a needle valve, and mixes with a measured flow (Sierra Instruments electronic flow controller, flow of 25.9 scc/s) of dry air. After waiting a few minutes for the system to stabilize, the metered HCl is shunted into a calibrated volume (149.25 ± 0.5 cm³) and the rate of pressure rise in this volume is measured

using a 10 torr capacitance manometer (Baratron, 0.15% accuracy) and a digital stopwatch. The flow of gas into this volume is related to the rate of pressure rise by

$$\Phi(\text{scc/s}) = \frac{\Delta P(\text{atm})}{\Delta t(\text{sec})} \frac{273}{T(\text{K})} \times \text{Volume}(\text{cm}^3) . \quad (11)$$

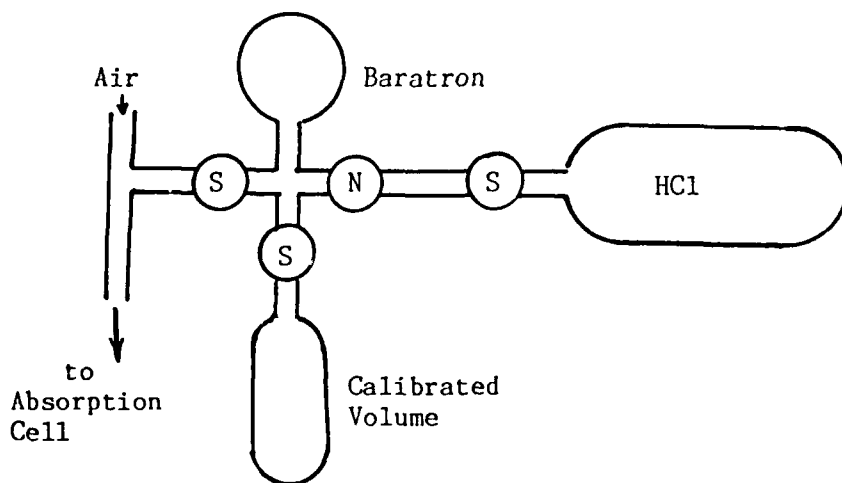


Figure 4. dP/dt Flow Calibration Apparatus for HCl.
S = shutoff valve; N = needle valve.

The resulting HCl flows ranged from 1.94×10^{-4} to 4.62×10^{-3} scc/s, equivalent to a range of 7.5 to 179 ppm HCl. The accuracy of these measurements is estimated at 2%, limited by the dry air flow reading from the electronic flowmeters. Measurement of the HCl flow rate was made before and after each run.

Interferences from other gases with absorption bands in the same $1.2 \mu\text{m}$ spectral region could potentially arise if an absorption line of the interfering gas happens to overlap the chosen HCl analysis line. Weak lines of carbon dioxide and water vapor are known to exist in this general spectral region, although the high resolution Air Force Geophysics Laboratory line parameters compilation²² does not indicate any interference between these species. We checked directly for potential interferences from H_2O and CO_2 by

introducing large concentrations of these species into the absorption cell (approximately 20 torr pure H₂O and 50 torr pure CO₂) and scanning the laser wavelength to locate absorption lines from these species. While weak lines due to both species were observed, none of these lines overlaps the HCl absorption line which we chose for this study. Therefore, the instrumentation will not experience interferences due to either H₂O or CO₂. No other atmospheric species is naturally present at sufficient concentration to pose a potential interference. In any case, due to the very high spectral resolution of the technique, an interference-free HCl absorption line should be available even if other potential contaminants are present at elevated levels after missile launches.

4. RESULTS

4. HCl Absorption Line Parameters

Prior to conducting detailed measurements, preliminary experiments were performed to identify appropriate laser operating parameters for measurement of a suitable absorption line of HCl. A temperature survey showed that at least five HCl absorption lines could be detected in the laser temperature range between 0 °C and 20 °C. The strongest HCl signal was obtained by operating the laser at a temperature of 8.7 °C, and all further measurements were conducted at this laser temperature. The laser wavelength for this operating condition was determined to be $1.208 \pm .0004 \mu\text{m}$ using a monochromator. By reference to the tabulated HCl second overtone line positions in the Air Force Geophysics Laboratory infrared line parameters compilation,²² this line is the P(3) line of H^{35}Cl at 8278.7 cm^{-1} ($1.2079 \mu\text{m}$). It is believed that the other lines observed in our laser temperature survey included the P(4) H^{35}Cl line and the P(2), P(3), and P(4) lines of H^{37}Cl .

The absolute calibration of hydrogen chloride gas measurements using the infrared diode laser absorption technique is based on the accurate measurement of infrared line strength and line broadening. Once these parameters are accurately known, then determination of the HCl concentration under sampled conditions requires only a measurement of the fractional absorption and the cell temperature and pressure. Knowledge of these parameters is also essential for determining the optimum measurement conditions and analyzing the ultimate sensitivity of the technique. Although calculated line strength and broadening parameters are tabulated in the AFGL compilation, these parameters are based on thirty-year old experiments employing low resolution infrared absorption techniques.²³ Thus, we undertook measurements of line strength and air broadening coefficient for the P(3) line of H^{35}Cl . The techniques employed in these measurements were previously discussed in Section 3.3.2.

The Voigt line profile fitting procedure was used to analyze the line strength and line broadening data. Figure 5 shows a comparison of a measured and fitted absorption profile for the H^{35}Cl P(3) line. The measurement conditions are given in the figure caption. Also plotted are the residuals

(the difference between the experimental profile and best Voigt fit), which appear random and are generally less than 3 percent of the peak of the profile.

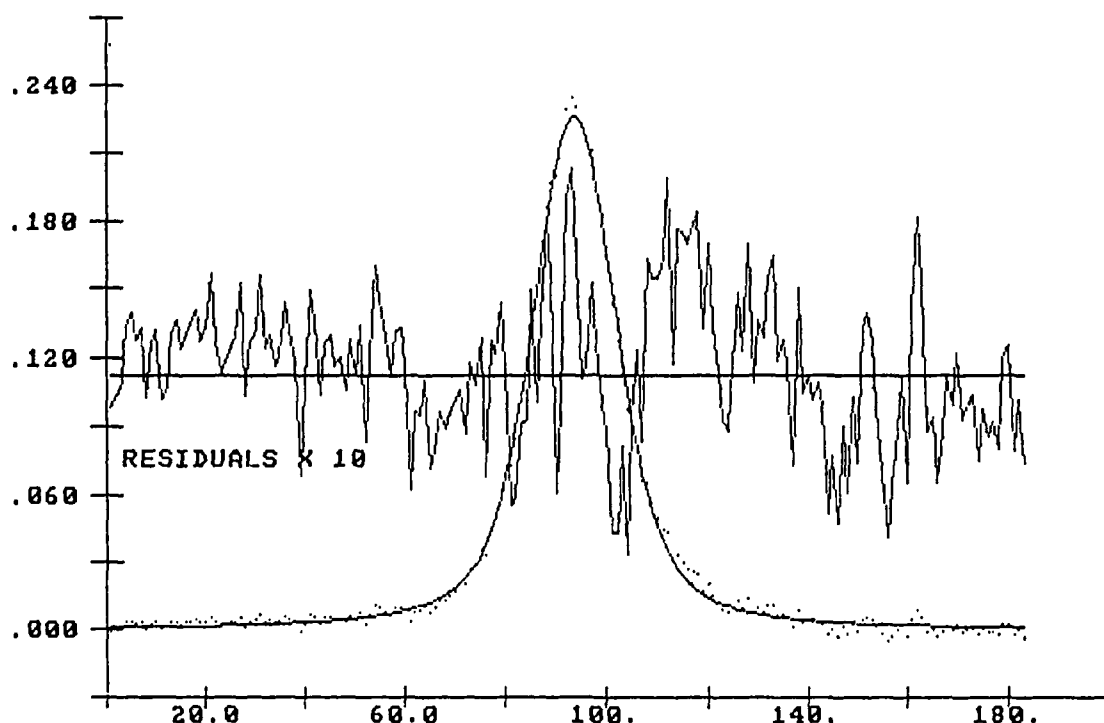


Figure 5. Experimental Absorption Data of HCl Broadened by 58 Torr of Air after Background Removal by Computer. Dots are observed data; solid curve is least-square fit using Voigt profile. Residuals enlarged by a factor of ten are displayed across the middle of the profile.

The experimental results obtained in measurement of the integrated line strength and air broadening coefficient for the HCl absorption line are indicated by the plots of reduced data shown in Figs. 6 and 7. Figure 6 is a plot of the integrated absorbance, obtained from the Voigt analyses, versus HCl pressure. The data points are fit by a weighted linear least squares procedure, where the estimated error in individual data points is due primarily to noise in the individual measurements. The slope of this linear fit, divided by the known path length of 1546 ± 3 cm (corresponding to 34

passes in the Herriott cell), yields an integrated line strength at 294 K of $(6.50 \pm 0.53) \times 10^{-23} \text{ cm}^2 \text{ molecule}^{-1} \text{ cm}^{-1}$. The overall experimental uncertainty of 8.2% is due mainly to precision errors (due to noise and background level uncertainties of 6.5%) and a possible systematic error in the relative calibration of the frequency scale in the spectra (estimated at 5%). This experimental uncertainty could probably be reduced to the 1 to 2 percent range by use of a single mode laser, permitting better radiometric accuracy, and by using an etalon to provide more accurate calibration of the frequency scale.

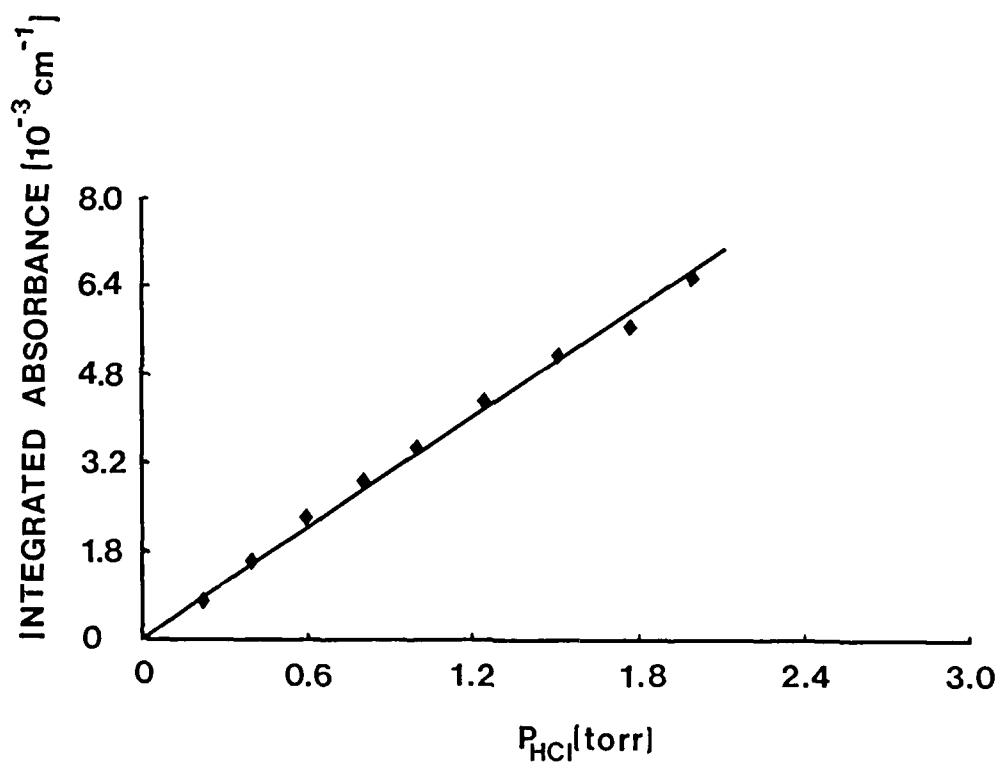


Figure 6. Plot of Integrated Absorbance vs. HCl Pressure for the P(3) Line of the Second Overtone Band of H^3Cl (path length = 1546 cm).

The Lorentz half widths for the same HCl line, obtained from the Voigt analyses, are plotted versus partial pressure of dry air in Fig. 7. A weighted linear least-squares fit yields the result $\gamma = 0.0636 \pm 0.0047 \text{ cm}^{-1} \text{ atm}^{-1}$ for the pressure-broadened halfwidth at half maximum.

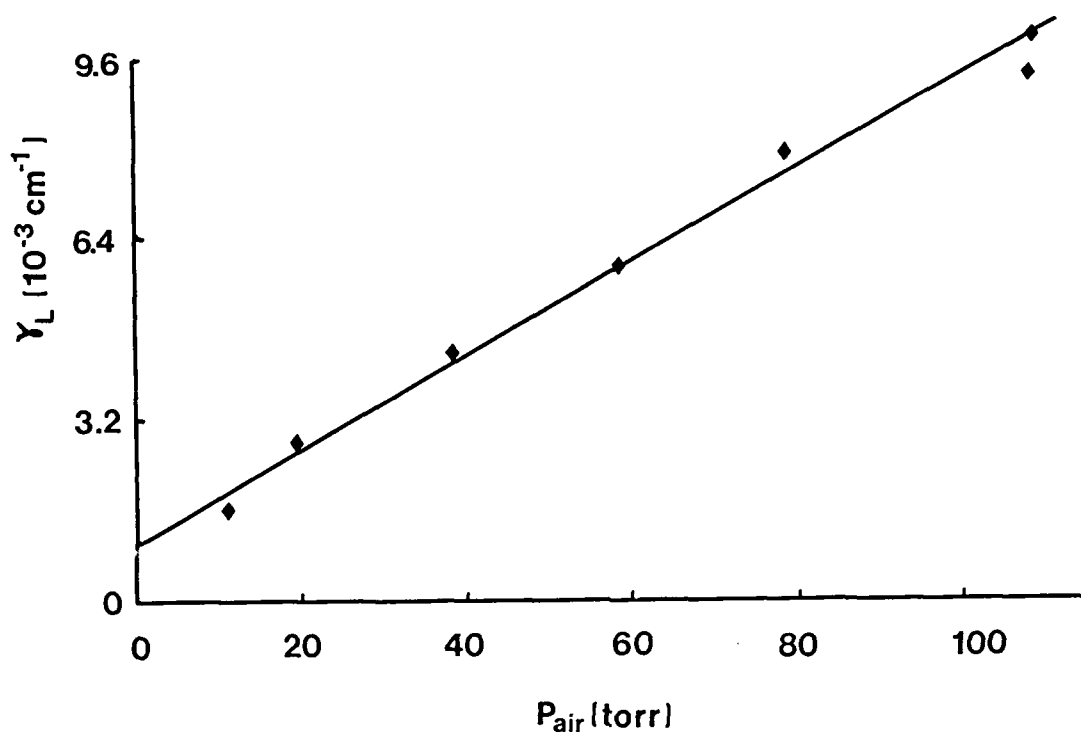


Figure 7. Plot of Lorentz Halfwidths vs. Broadening Gas Pressure.

The measured line strength may be compared with the previous result of Benedict et al.,²³ who used a low resolution infrared absorption method. These earlier experiments relied on linewidth measurements in the fundamental ($1 \leftarrow 0$) band, rather than direct linewidth measurements in the second overtone ($3 \leftarrow 0$) band, to obtain line strengths from the measured "equivalent widths." The result for the H^{35}Cl P(3) line, corrected to 294 K from Benedict's reported value at 300 K, is $S(294 \text{ K}) = 5.49 \times 10^{-23} \text{ cm}^2 \text{ molecule}^{-1} \text{ cm}^{-1}$. Although no uncertainty estimates are provided for the individual line strength measurements, the probable error quoted by Benedict for the $3 \leftarrow 0$ band strength is 10%. Since the band strength is, in effect, a weighted average of many line strength measurements, we might assume that the error in an individual measured line strength in these low resolution experiments is larger than 10%. Our measured value of $S(294 \text{ K}) = (6.50 \pm 0.53) \times 10^{-23} \text{ cm}^2 \text{ molecule}^{-1} \text{ cm}^{-1}$ is therefore not completely inconsistent with the Benedict result, but it does suggest that the earlier measurement is low.

We are not aware of previous measurements of HCl collisional broadening in the second overtone band. The measured broadening coefficient for the H^{35}Cl P(3) line in air of $0.0636 \pm 0.0047 \text{ cm}^{-1} \text{ atm}^{-1}$ is somewhat lower than the value of $0.0724 \pm 0.0006 \text{ cm}^{-1} \text{ atm}^{-1}$ obtained recently by Pine and Looney²⁴ for air broadening of the P(3) line in the fundamental band of H^{35}Cl , though some vibrational dependence of broadening coefficients is expected. The work of Pine and Looney demonstrated that collisional narrowing effects are significant in air broadening of HCl fundamental lines. In the present study, the noise in the direct transmission line profiles was substantially higher than in the work of Pine and Looney, primarily due to the need to fit both the 100% and 0% transmission baselines as well as the smaller effective absorbance levels due to the weaker transitions and the multimode nature of the laser. The residual errors between the calculated Voigt fits and the data appeared random and within the measurement noise levels. Therefore, the present experimental precision does not justify the use of a more sophisticated line profile model²⁵ which accounts for the effects of collisional narrowing.

4.2 Studies of Detection Sensitivity

4.2.1 Two-Tone FM Performance

Two-tone spectra were taken for a range of HCl concentrations in the absorption cell. This detection method proved to be very easy to implement and the resulting spectral waveforms were in accord with those predicted by theory. An example of a two-tone spectrum is shown in Fig. 8a for 2 torr of HCl in 50 torr of air. Notice the flat baseline and symmetry of the two downward peaks about the center frequency. It can be shown that the difference in height between the upper and lower peaks is approximately equal to $0.5\alpha_0\beta^2 I_0 \cdot \exp[-\alpha_0]$. By independently making a direct absorption measurement under the same experimental conditions one can exactly determine I_0 and α_0 , permitting the approximate value of β to be found. Similarly, Cooper and Watjen¹⁸ have shown that the ratio of the difference in the amplitude of the two downward peaks to their sum is approximately equal to $(2M/\beta)\sin\psi$. As seen in Fig. 8a, this ratio is very small, and a magnified scan of the peak region provides the sensitivity required to measure M , provided the value of ψ is known. The phase difference between the AM and FM

modulation, ψ , has been found by Lenth to be $\sim \pi/2$ for $\omega_m < 750$ MHz using a GaAlAs diode laser,¹⁵ and previous results obtained with a lead-salt diode laser also indicate $\psi \approx \pi/2$.¹⁹ If we assume this value for ψ , then M can be estimated since β has been measured.

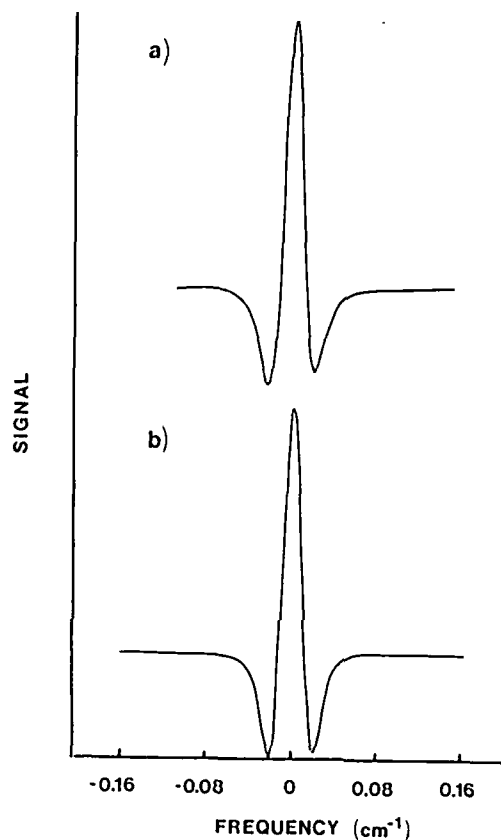


Figure 8. Two-Tone FM Spectrum of HCl. a) Measured; b) Calculated.

Using these estimated values for β and M as starting points, along with the previously measured broadening coefficients, detailed parametric computations of line shapes were performed. The parameters M and β were varied to optimize the shape and magnitude of the calculated line shape in comparison with the measured waveform. The result of these calculations is shown in Fig 8b. The values for M and β obtained in this analysis are 0.0052 and 0.39, respectively. This procedure was repeated for a number of scans, and the error in these parameters is estimated at less than 10 percent. With the FM detection parameters established, spectral measurements of mixtures

containing unknown amounts of HCl can be made and the measured peak heights directly related to absolute concentration values.

4.2.2 Measurements of Low HCl Concentrations

As described in Section 3.3.4, the sensitivity of the Phase I diode laser instrumentation for HCl detection was analyzed by direct measurement of low-concentration flows of HCl in air. An example of experimental data for an HCl concentration of 7.5 ppm is shown in Fig. 9. Figure 9a shows the raw two-tone FM signal as recorded with the lock-in amplifier using a 0.3 second time constant. The HCl signal appears on a strongly sloping baseline. This signal disappeared when the HCl flow to the cell was shut off. The baseline slope is due to the carryover of laser intensity variations into the FM signal due to the residual amplitude modulation effect. (This baseline is the $2I_0M^2$ term discussed in Section 3.3.3.1.) In spite of the baseline variation, the HCl signal is obvious. Figure 9b shows the same 7.5-ppm HCl signal after computer subtraction of the sloping baseline and smoothing of the data using a procedure which does not degrade the wavelength resolution.²⁶ Such computer processing is not necessary to identify the HCl signal but was performed in this instance to illustrate that the signal still exhibits the characteristic two-tone FM line shape.



Figure 9. Two-tone spectrum of 7.5 ppm HCl. a) Raw data;
b) Digitized data and computer-smoothed curve.

The linearity of the FM signal as a function of HCl concentration is demonstrated in Fig. 10. The lack of an intercept at zero HCl concentration demonstrates that outgassing or adsorption of HCl at the cell walls is insignificant under these measurement conditions. The minimum detectable HCl concentration may be determined by fitting the FM signal dependence to a straight line and equating the resulting relationship to the noise level in the FM signal, i.e. for $S_{FM} = b[HCl]$, we obtain $[HCl]_{min} = N_{FM}/b$, where N_{FM} is the FM noise level. From this analysis, we obtain $[HCl]_{min} = 3$ parts per million for our Phase I experiments. This noise level is equivalent to a fractional absorption of 1.8×10^{-5} of the laser mode intensity coincident with the HCl line and 4.0×10^{-6} of the total multimode laser power.

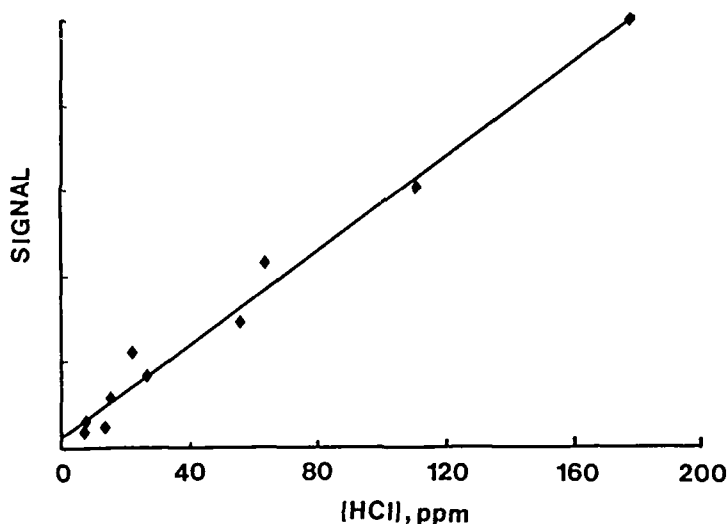


Figure 10. Plot of FM Peak Signal Versus HCl Concentration.

The significance of this result is that we have directly demonstrated a detection limit of 3 ppm for a nonoptimized instrument design. By comparison of theoretical signal to noise (S/N) calculations with the experimentally attained S/N, we can understand how the sensitivity can be improved. This comparison, and a description of approaches which can be taken to optimize the sensitivity to below the 0.1 ppm level, is described below.

4.2.3 Comparison with Theoretical Sensitivity Limits

From Beer's law, one can represent the absorbance α as the product of the absorption cross section σ , absorbing gas number density N , and path length l . Using this expression and the determination of α_{\min} (using either Eqs. 7 or 10), one can calculate the minimum detectable number density (N_{\min}). This result can also be expressed as a fractional concentration by

$$[\text{HCl}]_{\min} = N_{\min}/N_{\text{total}} , \quad (10)$$

where the total gas concentration can be found from the total gas pressure P .

For a germanium detector with a quantum efficiency of 0.52, $R_L = 50$ ohms, a bandwidth of 1 Hz, and $T_N = 295$ K, the minimum detectable absorption can be computed as a function of various system parameters such as laser power, M , β , and modulation frequency. The present calculations set the laser excess noise at a value consistent with the 5×10^{-3} relative noise level which was observed in direct absorption measurements. One finds that, at higher powers and $M \neq 0$, the sensitivity is limited by the laser excess noise and varies as $1/M^2$, whereas at lower powers α_{\min} is controlled by either the shot-noise or detector thermal noise, depending on the particular situation. Maximum sensitivity is also obtained with $\beta = 1.15$. In these Phase I experiments, the theoretical minimum detectable absorption level for our laser power and modulation conditions (780 μW at the detector, $\beta = 0.39$, and $M = 0.0052$) is about 1.2×10^{-5} . This computation takes into account the multimode character of the laser, where only the single mode portion of the total laser power contributes to the signal while the total power contributes to the noise. This calculation compares quite favorably with our measured minimum detectable absorption (at a 3 Hz bandwidth) of about 1.8×10^{-5} . This experimental value is equivalent to 1.0×10^{-5} at a bandwidth of 1 Hz.

4.2.4. Optimization of Detection Sensitivity

The preceding discussion showed that one can indeed achieve detector-limited sensitivities using two-tone FM detection, corresponding to an HCl concentration of about 3 ppm in these experiments. However, this limit depends on a number of parameters which can be controlled to some extent, and

could be significantly improved by making a few changes in the existing system.

First, β can be optimized to a value of 1.15 by a small amount of amplification and by better impedance matching of the rf modulation signal to the laser injection current. In this Phase I program, optimization of β was not considered, and the rf current was simply coupled to the injection current through a small capacitor. The signal is proportional to β^2 , and thus optimizing β would increase the signal by a factor of nine.

For a given fractional concentration of HCl in air, the absolute concentration of HCl in the cell is simply linearly proportional to the cell pressure. This implies that it is desirable to work at the highest pressure possible, i.e. at atmospheric pressure. However, the peak intensity of the absorption line shape is only proportional to total pressure (for fixed fractional HCl concentration) where pressure broadening is not important (i.e., in the low pressure Doppler regime). At higher pressures where pressure broadening dominates the line shape, the peak intensity becomes independent of pressure and the absorption halfwidth increases linearly with the pressure (thus maintaining the same integrated line strength). For the measured line of HCl, this means that the peak direct absorption signal maximizes at a constant value above about 250 torr. However, as mentioned earlier, if the modulation frequencies are not much greater than the absorption halfwidths, then the wings of the individual (negative) side lobe components begin to cancel the (positive) magnitude of the central peak (see Eq. 6). As a result, the FM signal will decrease if the pressure (hence linewidth) gets too large. The use of a higher modulation frequency, on the order of 1 to 2 GHz, would better separate the side lobes from the central peak, somewhat lessening this cancellation effect. Nonetheless, as a result of these competing effects, there is an optimum pressure for which the FM signal and detection sensitivity is maximized. This dependence of the FM signal versus system pressure is shown in Fig. 10 assuming a 2 GHz modulation frequency. The best sensitivity is achieved at about 300 torr, but if one desired to operate at atmospheric pressure for reasons of instrument design simplification, then only a 20% loss in optimum sensitivity would be encountered (using the local atmospheric pressure for White Sands).

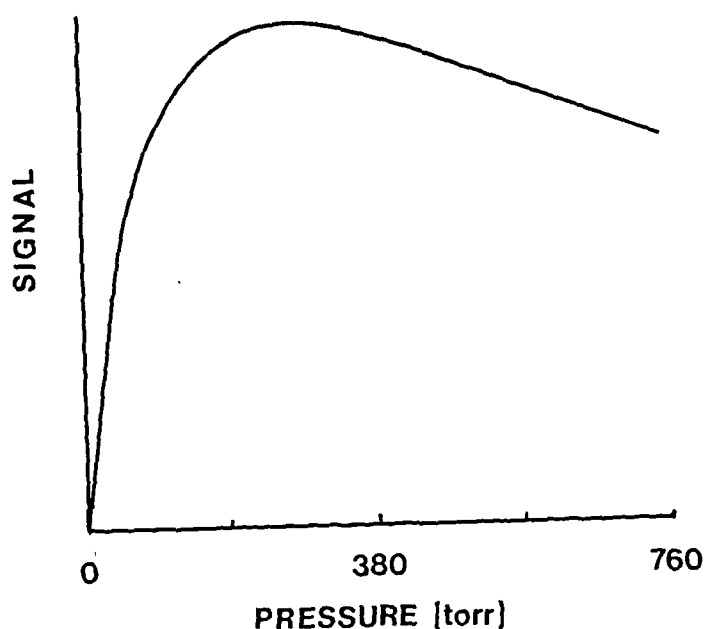


Figure 10. FM Signal Dependence on Cell Pressure.

Another improvement in sensitivity would be the use of a single mode (distributed feedback or external cavity) laser, instead of the multimode laser which was used in Phase I. (A single mode laser was not used in Phase I because of the limited time and budget.) This would make much more efficient use of the total output power and might also reduce the amplitude modulation noise, as there would be no mode competition or mode interferences in the power spectrum. One could also increase the optical absorption path length by a factor of three or so, by a combination of longer cell length and more optical passes of the cell. The laser power at the detector could be improved by using higher reflectivity mirrors in the multiple pass cell and by using higher power lasers as they become available.

The overall result of these straightforward improvements is an enhancement by at least a factor of 60 in the minimum detectable concentration level. If M also decreases as a result of using the single mode laser, then a further improvement, scaling as M^2 , is expected. None of these changes to the system are difficult to accomplish and detection limits of better than 0.05 ppm of HCl (with a response time of less than one second) should be readily attainable.

5. CONCLUSIONS AND RECOMMENDATIONS

All of the Phase I research objectives were achieved in the laboratory studies performed for this project. In particular, the feasibility of sensitive detection of hydrogen chloride gas with rapid time response using a near-infrared laser diode was established. A sensitivity limit of 3 parts per million HCl in air, with an integration time of less than one second, was demonstrated by direct measurement using breadboard instrumentation assembled for Phase I. An analysis of the signal to noise ratios achieved in these experiments shows that this sensitivity was in good agreement with theoretical expectations. This analysis also shows that substantial improvements in sensitivity can be achieved by an optimized design using an increased absorption path length, single mode laser operation, higher laser modulation frequencies, higher measurement pressures, and improved coupling of the rf modulation of the laser by proper impedance matching. By implementing these modifications, an improvement in sensitivity by at least a factor of 60 to 100 is expected, permitting the rapid measurement of HCl concentrations at levels well below 0.1 ppm. It is important to stress that none of these changes requires any kind of technological breakthrough, but rather they are simple extensions of already demonstrated designs and procedures.

A hydrogen chloride gas monitor based on this approach can therefore meet the requirements for HCl monitoring in missile launch areas, where sensitivity of 0.1 ppm and time response faster than one second are needed. These characteristics will be a substantial improvement over existing HCl monitors intended for real-time use, where either poor sensitivity or slow time response have imposed severe limitations. The approach also holds great promise for the development of a simple, rugged instrument design, using highly reliable and inexpensive laser diodes combined with fiber optics.

The continued development of instrumentation based on this concept would emphasize the design improvements described above in a system utilizing fiber optics to replace all conventional optics external to the absorption cell. The other area of design emphasis would be the development of a real time readout system, possibly incorporating an alarm indication, data logging, or other features to be determined by program requirements. The desired time

response of one second can be achieved even at the lowest concentrations of interest, provided that the system is designed for a gas throughput time of less than one second. An attractive feature of the FM detection method is that the signal is directly proportional to the HCl concentration, so that no complicated data reduction procedures are required.

In conclusion, this Phase I study has demonstrated the possibility of compact and sensitive instrumentation for real-time measurement of HCl concentrations in missile launch areas using reliable, low cost near-infrared laser diodes. Although this study has focused on detection of HCl, similar technology could be applied to develop instrumentation for many other gases in such applications as toxic gas detection, on-line monitoring of industrial processes, pollutant monitoring, etc.

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